

**PREPARATION AND CHARACTERIZATION OF OPAQUE DENTAL
PORCELAIN POWDER AS A FILLER IN DENTURE BASE POLY (METHYL
METHACRYLATE)**

by

ASAM M.A. ABUDALAZEZ

**Thesis submitted in fulfillment of the
requirements for degree of
Master Science**

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LIST OF SYMBOLS

a	:	Notch Length
α	:	Face Angle of Indentation
A_s	:	Surface Area of Indentation
b	:	Width
c	:	Composite
d	:	Thickness
d_1	:	Density of Water at 25 °C
E	:	Elastic Modulus
GPa	:	Giga Pascal
K	:	Boltzmann Constant
Kgf	:	Kilogram-Force
KIc	:	Fracture Toughness
kV	:	Kilo Volt
L	:	Length
m	:	Tangent of the Initial Straight Line of Load Versus Deflection Curve
m	:	Matrix
μm	:	Micrometer
MPa	:	Mega Pascal
n	:	Order
P	:	Load
P	:	Weight of Pycnometer with Cover
ρ	:	Density
pH	:	Acidity Measurement
t	:	Specimen Thickness
T	:	Absolute Temperature
V_f	:	Volume Fraction
W	:	Weight of Pycnometer, Cover and Dry Sample
W_1	:	Weight of Pycnometer, Cover and Distilled Water
W_2	:	Weight of Pycnometer, Cover, Distilled Water and Sample
W_f	:	Weight Fraction

γ	:	Correction Factor
σ		Tensile Strength
λ	:	Wavelength
θ	:	Half of the Angle of Diffraction
γ -MPS		3-(Trimethoxysilyl) Propyl Methacrylate or 3-(Methacryloxy) Propyl Trimethoxysilane

LIST OF ABBREVIATION

ANOVA	:	One Way Statistical Analysis
BIS-GMA	:	Bis-(2-Hydroxypropyl)-Methacrylate
BPO	:	Benzoyl Peroxide
CAD	:	Computer-Aided Design
CAM	:	Computer-Aided Manufacturing
DSC	:	Differential Scanning Calorimetry
EDS	:	Energy Dispersive X-Ray Spectroscopy
EGDMA	:	Ethylene Glycole Dimethacrylate
FTIR	:	Fourier Transform Infra Red Spectroscopy
GPS	:	Glycidoxypropyl Trimethoxy Silane
HA	:	Hydroxyapatite
HDPE	:	High Density Poly Ethylene
HIPS	:	High Impact Polystyrene
ISO	:	International Standardization Organization
L.O.I.	:	The Value of Loss on Ignition
MHz	:	Mega Hertz
MMA	:	Methyl Methacrylate
MW	:	Mega Watt
OD	:	Optical Density
ODP	:	Opaque Dental Porcelain
PFM	:	Porcelain-Fused-to-Metal
P/L	:	Powder to Liquid Ratio
PMMA	:	Poly(methyl methacrylate)
ppm	:	Part Per Million
SBF	:	Simulated Body Fluid
SEM	:	Scanning Electron Microscope
SEN-B	:	Single Edge Notch Bending Test
S.G.	:	Specific Gravity
TGA	:	Thermogravimetric Analysis
UV	:	Ultra Violet
VHN	:	Vickers Hardness Number

XRD : X-Ray Diffraction
XRF : X-Ray Fluorescence

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PENYEDIAAN DAN PENCIRIAN SERBUK PORSELIN GIGI LEGAP SEBAGAI BAHAN PENGISI DI DALAM TAPAK GIGI PALSU POLI(METILMETAKRILAT)

ABSTRAK

Serbuk porselin gigi legap sebagai bahan pengisi seramik dimasukkan ke dalam matriks PMMA untuk mengkaji komposit yang terhasil dari segi sifat fizikal, mekanikal, terma, persekitaran dan radiopasiti serta menilai kesesuaiannya digunakan sebagai bahan restorasi gigi. Benzoin peroksida (BPO) digunakan sebagai bahan pemula, sementara MMA ialah monomer yang digunakan dan EGDMA sebagai agen sambung-silang. Porselin gigi legap disediakan melalui peleburan bahan mentah pada suhu 1350°C selama 2 jam dan diikuti dengan proses lindapkejut di dalam air sejuk untuk membentuk frit. Frit dihancurkan menggunakan mesin pengisar untuk menghasilkan serbuk porselin yang melepasi penapis bersaiz 75 μm . Serbuk porselin gigi yang terhasil dirawat menggunakan agen pengganding silan (γ -MPS) sebelum digunakan sebagai bahan pengisi komposit. Tiga nisbah berat (5%, 10% dan 15%) untuk kedua-dua porselin dirawat dan tidak dirawat masing-masing ditambahkan ke dalam matriks (PMMA dan 0.5% BPO). Sampel-sampel telah diuji untuk sifat-sifat fizikal, mekanikal, terma, persekitaran (dalam Bendalir Badan Simulasi (SBF) dan radiopasiti. Bahan pengisi yang dirawat dengan agen coupling silan γ -MPS menghasilkan komposit yang menunjukkan peningkatan dari segi nilai tegasan, kekuatan patah, kekuatan patah dan ketegaran. Sampel-sampel yang dimasukkan pengisi tidak dirawat menunjukkan kekerasan yang lebih tinggi daripada sampel yang dirawat. Keadaan ini dapat dikaitkan secara positif dengan kelakuan kekuatan patahnya. Suhu degradasi lebih tinggi untuk sampel-sampel yang mempunyai pengisi berbanding sampel yang tiada pengisi. Sampel yang mempunyai pengisi juga menunjukkan kurang melarut di dalam air (lebih rendah daripada nilai yang ditetapkan oleh piawaian ISO 1567-2000 untuk bahan tapak gigi palsu). Sampel yang berpengisi terawat menunjukkan lebih rendah penyerapannya dan sangat sedikit kehilangan berat berbanding sampel yang tidak dirawat. Sampel yang berpengisi menunjukkan kelakuan radiopasiti yang tidak begitu ketara yang disebabkan tiada logam-logam berat yang hadir.

PREPARATION AND CHARACTERIZATION OF OPAQUE DENTAL PORCELAIN POWDER AS A FILLER IN DENTURE BASE POLY (METHYL METHACRYLATE)

ABSTRACT

Opaque dental porcelain powder as ceramic filler incorporated into PMMA matrix was carried out to test the resulted composite in terms of its physical, mechanical, environmental and radioopacity qualities for the applicability in dental restoration. Benzoyl peroxide (BPO) was used as initiator while MMA was used as monomer and EGDMA as the cross-linking agent. Opaque dental porcelain was prepared through melting the raw materials at 1350°C for 2 hours, quenching in cold water to form frit. Frit was crushed in a milling machine and the resulted product was sieved to pass the size of 75 μm . The opaque dental porcelain powder was treated with silane coupling agent (γ -MPS) before it was incorporated into a solid components (PMMA, BPO). Three different ratios (i.e. 5%, 10% and 15% by weight) of treated and untreated fillers were added into the matrix (PMMA and 0.5% BPO), respectively. Samples were tested for physical, mechanical, thermal, environmental (using Simulated Body Fluid Absorption, SBF) and radiopacity properties. Filler treatment by γ -MPS had resulted in improving the tensile, fracture toughness, flexural, and stiffness of the composite. The filled samples had shown also higher hardness values than that of the untreated samples, positively correlated with the fracture toughness. The degradation temperature of the filler-filled PMMA samples had shown slightly higher than that of the unfilled samples. The filler-filled formulations showed less water solubility (below the values of ISO standards), less absorption and reduced weight loss than that of the untreated samples. The filled samples had shown insignificant radiopacity.

CHAPTER 1 INTRODUCTION

1.0 Background

The overriding goal of dentistry is to maintain or improve the quality of life of the dental patient. This goal can be accomplished by preventing disease, relieving pain, improving mastication efficiency, enhancing speech, and improving appearance. Because many of these objectives require the replacement or alteration of tooth structure, the main challenges for centuries have been the development and selection of biocompatible long-lasting, direct-filling tooth restoratives and indirectly processed prosthetic materials that can withstand the adverse conditions of the oral environment (Anusavice, 2003). Historically, a wide variety of materials have been used as tooth crown and root replacements, including animal teeth, bone, human teeth, ivory seashells, ceramics, and metals. Restorative materials for the replacement of missing portions of tooth structure have evolved more slowly over the past several centuries.

Dental materials may work as preventive, restorative or auxiliary roles. The four groups of materials used in dentistry today are metals, ceramics, polymers, and composites. Despite recent improvements in the physical properties of these materials, none of these are permanent. Dentists and materials scientists will continue the search in the 21st century for the ideal restorative material. An ideal restorative material would (1) be biocompatible (2)

bond permanently to tooth structure or bone, (3) match the natural appearance of tooth structure and other visible tissues, (4) exhibit properties similar to those of tooth enamel, dentin, and other tissues, and (5) be capable of initiating tissue repair or regeneration of missing or damaged tissues (Anusavice, 2003).

Polymers have a major role in most areas of dentistry. Their distinctive properties allow a range of clinical applications not possible with other types of materials. The most widely used impression materials as polymers are, for example, alginates, polyethers, polysulfides, and silicones. A polymeric matrix with particulate ceramic filler is the most commonly used anterior esthetic restorative material. Additional applications include artificial teeth, cements, dies, temporary crowns, endodontic fillings, tissue conditioners, and pit and fissure sealants. However, the primary use of polymers in terms of quantity is in the construction of complete dentures and tissue bearing portions of partial dentures (Brien, 1997).

The ideal denture base material should possess several key physical attributes. Some of these properties include biocompatibility, good esthetics, high bond strength with available denture teeth, radiopacity, ease of repair, and should possess adequate physical and mechanical properties. The denture base must be strong enough to allow the prosthesis to withstand functional and parafunctional masticatory forces. In addition, because these prostheses are

removable, shock induced fracture resistance, possibly due to patient abuse, is desirable (Brien, 1997).

Many different materials have been used for denture bases. Historically materials such as bone, wood, ivory, and vulcanized rubber were utilized; now poly(methyl methacrylate) (PMMA) is used. New materials such as polystyrene and light-activated urethane dimethacrylate have been developed, but PMMA remains the preferred material for removable complete and partial prostheses. The popularity of PMMA materials is based on its low cost, relative ease of use, and reliance on simple processing equipment (Meng and Latta, 2005).

In the 1930, Walter Wright and Vernon brothers at the Rohm and Haas Company in Philadelphia developed PMMA, a hard plastic. Although many other materials were utilized for dental prosthetic none could come close to that of PMMA, and nowadays about 90-95 % of dentures are fabricated from this acrylic polymer (Ferracane, 2001). The popularity of PMMA is associated with its favorable working characteristics, processing ease, accurate fit, stability in oral environment, superior esthetics, and the ability to be used with inexpensive equipment (John et al., 2001). On the other hand, emerging from the exploding trend of applications of synthetic polymers is a growing need for nondestructive techniques to evaluate these polymer systems. X-ray and ultrasound radiographic imaging techniques are the most commonly used to evaluate materials and are fast, convenient, reliable, and nondestructive. However, until

recently these techniques were not sufficiently sensitive to detect polymers so that the physical changes that occur in polymer systems could be observed. The search for a nondestructive method of polymer evaluation has led to a new area of research, that of radiopaque polymers (Brauer, 1983).

1.1 Radiopaque Polymer in Denture Base Material

The study of radiopaque polymers has been based on empirical approaches that have led to more systematic investigation in the past few years. The establishment of a reliable, quick, nondestructive imaging method for detecting changes in polymer systems can benefit numerous industries such as dentistry. It is often necessary to detect polymeric materials when they are used in dentistry for prosthetic applications, such as dentures or restorative resins (eg, composite filling materials). Radiopaque polymers could be applied to composite materials under stress for detection of mechanical deficiencies such as cracks and crazes. The tested material with its radiopaque polymeric additive may also be exposed to weathering and aging conditions and radiographed. Low molecular weight compounds can interact with the tested material causing swelling or partially dissolving the tested specimen. Therefore, replacement of these low molecular weight compounds by radiopaque monomers polymerized *in situ* may prove advantageous. When added to the test material, polymers do not interact with and do not cause degradation of mechanical properties such as shear and tensile strength. This results in the superiority of the *in situ* polymerized additives over the nonpolymeric compounds used at present for the

imaging of mechanical defects. Based on casting shadows, radiographic imaging techniques incorporate the principle of radiopacity, which is the physical property of absorbing X-rays or reflecting ultrasound waves. Both techniques depend on variations in densities between a specimen and its surroundings. Sharp X-ray imaging is obtained from materials of high electron density; effective ultrasound is observed only when significant variations in specific gravity exist between an object and its surroundings (Mark et al., 1988).

1.2 Problem Statement

One of the most widely used materials in prosthetic dentistry is PMMA. Due to the fact that it has excellent appearance, ease in processing and repairability, PMMA is an excellent denture base material and is more stable in the mouth compared to any materials used before.

The thesis's approach for enhancing the physical and mechanical properties of denture base material is through the incorporation of ceramic filler opaque dental porcelain to act as reinforcement agent. The tested material can then be detected for mechanical behavior through radiopacity examination. However, the usage of opaque dental porcelain in denture base as reinforcement is not widely reported in open literature.

1.3 Research Objectives

- i. To prepare and investigate the effects of opaque dental porcelain as filler in PMMA matrix.
- ii. To study the effects of mixing method on the quality of porcelain filled PMMA composite.
- iii. To characterize the effect of silane coupling treatment on opaque dental porcelain filled PMMA composite.
- iv. To characterize the physical and mechanical properties of opaque dental porcelain filled PMMA composite.

1.4 Organization of the Thesis

Chapter 2 provides an overview survey of literature on the denture base materials and their role and properties in reference to widely relevant previous works that are closely related to this study.

Chapter 3 outlines the general methodology adopted in the research project. Discussion on the research flow chart and methods, tests and step-by-step experimental procedure employed in the study are given in detail. Description of lab equipments that used in generalizing the data is also given.

Chapter 4 aims at presenting and discussing the results and findings of the experimental works done and synthesizing the information on the usefulness of adopted treatment method in this study.

Chapter 5 highlights the conclusion and recommendations pertaining on the advantages and disadvantages of the adopted method, and suggestion for future work and further developments, as optimum fruits out of this research.

CHAPTER TWO LITERATURE REVIEW

2.0 Background

Modern dental practice has become very dependent on its materials, such that the dentist's greatest challenge is choosing the right combinations of them for the benefit of their patients (AZoM™, 2008). The science of dental materials involves a study of the composition and properties of materials and the way in which they interact with the environment they are placed in. The selection of materials for any given application can thus be undertaken with confidence and sound judgment (McCabe and Walls, 1998). Dental materials are used to replace the natural dentition or portions of it, to preserve existing dentition, or to strengthen or enhance the existing esthetic appearance. The oral cavity presents a unique and complex set of environmental characteristics; thus materials created to withstand the conditions found in the oral cavity must be developed with consideration of some of these unique factors (Dietz-Bourguignon, 2006).

Many dental materials are fixed permanently into the patient's mouth or are removed only intermittently for cleaning. Such materials have to withstand the effects of most hazardous environment. Variations in temperature, acidity or alkalinity and high stresses all have an effect on the durability of materials. Normal temperature variations in the oral cavity lie between 32°C and 37°C depending on whether the mouth is open or closed. The ingestion of hot or cold food or drink, however, extends this temperature range from 0°C up 70°C. The

acidity or alkalinity of fluids in the oral cavity as measured by pH varies from around 4 to 8.5, whilst the intakes of acid fruit juices or alkaline medicaments can extend this range from pH 2 to 11. The load on 1 mm² of tooth or restorative material can reach levels as high as many kilograms indicating the demanding mechanical property requirements of some materials (McCabe and Walls, 1998).

The dental materials selected for use as replacements for natural tissues place a very high demand upon the chemical, physical and biological properties. The materials must be (McCabe and Walls, 1998):

- i. Compatible with biological tissues and without eliciting any adverse reactions;
- ii. Capable of responding successfully to the stresses and strains;
- iii. Capable of withstanding the corrosive environment;
- iv. Capable of simulating in most cases the appearance of natural tissues, in terms of both color and translucency; and
- v. Capable of being reasonably easy to fabricate by traditional methods.

The first successful dental restorative material was gold followed by the use of dental porcelain. The first polymer to be successfully used as a denture base was vulcanite. Metals, ceramics and polymers have undergone significant developments in their adaptation for use as dental restorative materials (Cahn, et al., 1992). This chapter reviews these dental materials and gives an overview on the previous work done on these materials.

2.1 Definition of Biomaterials

A biomaterial is any substance (synthetic or natural) except drug, which can be used as a function of the body, or any materials, metals, ceramics, polymers, plastics or organics, brought into contact with fluids, cells, and tissue of living body. Examples of biomaterials are surgical implants and dental materials, dressing esthetics, prosthetic materials, and those used in extracorporeal circulation devices mentioned in the definition by Dorland Medical Dictionary (Anderson, 1994). Another definition for biomaterial is any material that constitutes parts of medical implants, extracorporeal devices, and disposables that have been utilized in medicine, surgery, dentistry, and veterinary medicine as well as in every aspect of patient health care. Dental biomaterial is that aspect of the subject, which considers materials for use in the mouth, as well as those employed in dental laboratory procedures. These biomaterials are used in the oral cavity either to restore function, comfort or aesthetics caused by developmental disorders, disease or trauma (Armstrong, 2006).

2.2 Biomaterials Used in Dentistry

Dentistry has the unique distinction of using the widest variety of materials. Biomaterials can be divided into two main classes: natural and synthetic biomaterials (Davis, 2003). Natural biomaterials are derived from animal and plants tissues. These materials are beneficial to the field of biomimetics in which they are used for implants similar and familiar to the body tissues. These materials do not offer problems of toxicity often faced by synthetic

materials. Biocompatibility is an important factor by which a dental biomaterial shows its ability to perform with appropriate response in a specific dental application (Lemons, 2004). Also, they may carry specific protein binding sites and other biochemical signals that may assist in tissue healing or integration, e.g. collagen used for bones, tendons, ligaments and skin in which it is implanted in a sponge form that does not have significant mechanical strength or stiffness. Other natural biomaterials are: corals, chitin (from insects and crustaceans), keratin (from hair) and cellulose (from plants). However, natural biomaterials can be subjected to problems of immunogenicity. Also, some natural polymers tend to denature or decompose at temperatures below their melting points. This severely limits their fabrication into implants of different sizes and shapes (Davis, 2003).

2.2.1 Ceramics

Ceramic materials have the ability to emulate natural teeth, and they are some of the oldest dental materials, going back to 1792, when complete dentures were made from them. In 1996 they are used to create inlays, veneers, and crowns, as facings on metal substrates, and even as bridges, which can be made completely from high-strength ceramics. Restorations in ceramics are generally made by building up the correct aesthetic combinations of pre-fired, pigmented particles, and then re-firing under vacuum to sinter them together and eliminate voids (AZoM™, 2008). Porcelain is a specific type of ceramic used extensively in dentistry and in other industries. Historically, the first use of porcelain was for

denture teeth. Later, all-porcelain crowns called "porcelain-jacket crowns" were developed for restoring anterior teeth that bore little or no occlusion. Ceramics are generally very brittle materials, which mean they cannot be bent or deformed to any extent without actually cracking and breaking. They are manufactured by fusing oxide powders together in furnaces at high temperature. Most pigmenting agents used in dentistry are metallic oxides. Their inclusion in appropriate ratios enables the ceramist to produce nearly any color imaginable. This quality also provides the dentist with the ability to match almost any tooth color with esthetic results that are unachievable with other materials (Ferracane, 2001).

Porcelain, a specific type of ceramic is essentially made from white clay (kaolin), quartz and feldspar. The ingredients are pulverized, blended, formed into shape and baked. This material is essentially the same as 'whiteware' used in industry for construction of tiles, sanitary ware etc. Kelly (1996) reported that Pierre Fauchard recognized the potential of porcelain enamels and initiated a research in porcelains to imitate the color of teeth and gingivae.

Glass ceramics are used extensively as reinforcing agents or fillers for dental composites. They also are used in several dental cements and temporary restorative materials. Because of their excellent biological properties ceramics are also used extensively as implant materials, either alone or as coating for metal substructures made from titanium that are placed directly into the mandible or maxilla (Ferracane, 2001).

Ceramics contain of metallic oxide compounds. Therefore, all ceramics have similar compositions. In any case, the main components of dental ceramics and porcelain are composed of quartz, feldspar and kaolin. Another important component of porcelain is leucite. Leucite is a crystalline potassium-aluminum-silica mineral that forms when feldspar and glass are melted together within the porcelain. Leucite is often added as a component because it strengthens, toughens, and raises the thermal expansion coefficient of normal feldspar porcelain. In addition to this glass modifier, pigments (metallic oxides) are added to porcelain for color (Ferracane, 2001).

Three types of porcelains are commonly used in dentistry. One particular type is used to make denture teeth. This porcelain is called "high fusing" because it fuses at approximately 1300°C to 1350°C. A second type of porcelain is known as low-fusing porcelain and has a fusion range of 850°C to 1050°C and is used as a veneer for metal in PFM restorations. A medium-fusing porcelain (fusing point of 1100°C to 1250°C) is used for the anterior porcelain jacket crown and has properties intermediate between those of the low and high porcelain types (Ferracane, 2001).

2.2.2 Metals

Metals have useful properties including strength, toughness and malleability and are commonly used in medicine and dentistry as implantable or prosthetic materials. They are easy to fabricate into usable form. Metals are stiff

and resilient with high modulus of elasticity and shear modulus combined with a high ultimate strength. Using alloys and special fabrication method process provides a wide range of options in selecting the best metals for a specific use (Ferracane, 2001). The metal titanium and a range of titanium alloys have received particular attention as dental and orthopedic implants. These materials tend to be well received by the body, which may be at least partially due to the relatively non-reactive surfaces. Titanium and titanium alloys have been developed as dental casting alloys. These metals are used with porcelain. Titanium is very reactive to oxygen and has a very high melting point. Therefore, special casting equipment is required in the production of dental prostheses from titanium. Although titanium has excellent biocompatibility, the extra effort and cost required to cast this metal has limited its use as dental restorative (Ferracane, 2001).

Metals find extensive use as structural components for the repair or replacement of tooth structure. Used specifically in the posterior region of the mouth where the metallic color is not objectionable, also be used more conservatively to replace portions of a tooth. When the portion of the tooth to be replaced is within the cusps, it called an inlay. When one or more cusps are included in restoration, but the entire crown is not replaced, it is called an onlay. Often the remaining teeth used as supports for metallic bridges that span the empty spaces to fill in the arch. These bridges are permanently fixed on the teeth with dental cement. Since they replace only a part of the dentition, they are often

called fixed partials (Ferracane, 2001). When a patient has several missing teeth, or when it is necessary to simulate lost gingival tissue with the dental prosthesis (often called a dental appliance), it is required a removable partial denture. The metal clasps are an extension of metal body or structural component of the removable partial denture, which provides it with strength and stability.

2.2.3 Polymer

A polymer is a large molecule comprised of repeating structural units, called monomers, joined by covalently bonds. "Poly" comes from the Greek word for "many" and "mer" comes from the Greek word for "parts." Polymer materials can be classified as inorganic and organic. Polymers are characterized as natural or synthetic and as homopolymers or copolymer. Copolymers and terpolymers are further classified according to the method of production and the arrangement of the monomeric units (Rosato et al., 2000). Synthetic polymers today find application in nearly every industry and area of life. Polymers are widely used as adhesives and lubricants, as well as structural components for many products, such as dentures (Harry et al., 2003). Brien (1997) stated that the primary use of polymers in terms of quantity is in the construction of complete dentures and the tissue-bearing portions of partial dentures. Polymers, such as PMMA, have ease of bond rotation which can occur under appropriate conditions are in contrast to rigid rod polymers where ease of bond rotation is highly limited at any reasonable temperature at which the system would be used or processed. Also, their

molecular system under a given set of conditions depends on a balance of three types of energy (Wilkes, 2002):

- i. Intramolecular, related to energy changes involved with bond rotations within the backbone and other types of intramolecular interactions between atoms or groups within the same molecule;
- ii. Intermolecular, results from the energies concerned with secondary bonding between groups or atoms or different molecules; and
- iii. Thermal energy, which is dictated by the product KT , where K is the Boltzmann constant and T is absolute temperature.

The lower the energy the more flexible the chain is and the easier it will be for it to undergo changes in its conformation.

Polymers are used extensively as temporary restorative materials for single restoration and bridges to be worn while the permanent metallic or ceramic restoration is being fabricated by laboratory. They are used as an adhesive agent to enhance the bonding between various materials and tooth structures or as sealants of pits and fissures present on the occlusal surfaces of permanent teeth (Ferracane, 2002).

2.2.4 Composites and Fillers

A composite material is a compound of two or more materials consisting of at least three structures; material A and B plus a bound interface AB (Szycher,

1992). Bhat and Nandish (2006) defined composites as the compound of two or more distinctly different materials with properties that are superior or intermediate to those of the individual components/constituents. Composite materials are attractive in biomaterial applications because these can mimic natural load transmitting structures, such as dental structures (Wintermantel et al., 2007). The most successful composite biomaterials used in dentistry as restorative material or dental cements are such as BIS-GMA quartz/silica filler and PMMA-glass fillers (Davis, 2003). Dental composites likely offer the best possibility for developing replacement materials provided superior characterization and low cost compared with dental ceramic and metal alloys (Ruddell et al., 2002). Using ceramic in a composite material raises the toughness of the product (Clyne and Jones, 2007) while using fillers will extend a material and reduce its cost (Concise Encyclopedia of Polymer Science and Technology, 2007). Generally, dental composites comprise three phases (Wintermantel et al., 2007):

- i. an organic phase, the matrix;
- ii. a dispersed phase, the fillers, e.g., particles or fibers; and
- iii. an interfacial phase, the coupling agents

The properties and volume fraction of individual phases are important for composites. Usually the matrix phase is the continuous phase and the other phase is said to be the dispersed phase. Based on the nature and shape of the dispersed phase, composites are often classified into particle-reinforced, whisker-reinforced or fiber-reinforced composites (Askeland and Phulé, 2003).

The matrix material generally starts out as a paste or liquid and begins to harden when it is activated, either by adding a catalyst (which may be mixed with the filler particles), or by adding water or another solvent to allow chemical reactions to take place. Before it hardens, it can be pressed into a mold, or stuffed into a hole.

Fillers (the dispersed phase) are classified according to their source, function, composition and/or morphology (Concise Encyclopedia of Polymer Science and Technology, 2007). They are differentiated by certain characteristics such as particle size and distribution, geometry and surface area. The filler particles can be of any coarseness varying from large rocks to microscopically fine powder or virtually any shape varying from spherical through fibers to flakes. Harper (2000) described that particles of smaller size achieve better properties enhancement compared to particles of larger dimensions. To ensure bonding between the filler and the matrix, the filler particles are coated with a silane-coupling agent that contains a methacrylic group able to co-polymerize with the matrix. Generally, according to filler particle size, dental composites may be classified into four categories as shown in Table 2.1.

Table 2.1: Classification of Composites According to Filler Particle Size (Bhat and Nandish, 2006)

Category	Filler Particle Size
Macrofilled composite (conventional/traditional composite)	8-12 μm
Small particle composite	1-5 μm
Microfilled composite	0.04-0.4 μm
Hybrid composite	0.6-1 μm

The properties of filler-filled polymers are determined by the properties of the components, by the shape of the filler phase, by the morphology of the system, and by the polymer-filler interfacial interactions (Concise Encyclopedia of Polymer Science and Technology, 2007).

2.3 Denture Base Material

Denture base is the part of a denture that rests on the oral mucus membrane and to which teeth are attached. It does not include the artificial teeth. Prior to 1940, vulcanite rubber was used as denture base material but it was difficult to pigment and tended to become unhygienic due to the uptake of saliva. Currently, acrylic resin, PMMA is used almost universally for denture base fabrication (McCabe et al., 2002). The ideal denture base material should possess several key physical attributes important in the fabrication of polymeric denture base as the cured polymer should be stiff enough to hold the teeth in occlusion during mastication and to minimize uneven loading of mucus. Some of these properties include biocompatibility, good esthetics, high bond strength with available denture teeth, radiopacity, ease of repair, and should possess adequate physical and mechanical properties. The denture base must be strong enough to allow the prosthesis to withstand functional and parafunctional masticatory forces. In addition, because these prostheses are removable, shock induced fracture resistance, possibly due to patient abuse, is desirable. The material should not deteriorate in the aqueous environment of the mouth and should be able to withstand attacks from solvents present in food, drinks, or

medications. The cured polymer has to be biologically inert and possess a low rate of foul smell formation and emission when in contact with other solvents (McCabe et al., 2002).

During fabrication of a denture, the curing conditions and choice of materials have great influence on the denture's subsequent physical and mechanical properties. Each curing cycle or fabrication technique is a compromise that attempts to optimize the properties for a given application. For an allergy prone patient, low residual monomer content in denture base has greater priority than stiffness. For a patient requiring a soft lining, stiffness is very important if the reduced cross-sectional area of the denture is not to cause stability or loading problems (O'Brien, 2002).

Dentists and manufactures of denture base materials have long sought for ideal materials and designs for dentures. So far, the results have been noteworthy although there are still some physical and mechanical problems with these materials. Dentures with good aesthetic qualities that are chemically and biologically inert can be easily constructed; nevertheless, functional failure still occurs. Acrylic resin is the most common denture base material used today. Acrylic resin is a plastics (resin) generated through chemical reaction by applying polymerization initiator and heat to a monomer. The chemical name for the resin produced from MMA is PMMA. It is sold by the trade names Plexiglas, Limacryl, R-Cast, Perspex, Plazcryl, Acrylex, Acrylite, Acrylplast, Altuglas, Polycast,

Oroglass and Lucite and is commonly called acrylic glass or simply acrylic. It is often preferred because of its moderate properties, easy handling and processing, and low cost, but behaves in a brittle manner when loaded. One of the main characteristic features of PMMA is its high transparency. With its high weather resistance, it does not easily turn yellow or crumble by sunlight (Wikipedia, 2008a). Memon (1999) stated that dentures made from acrylic resins are easy to process using inexpensive techniques and are esthetically pleasing.

2.3.1 Classification of Polymeric Denture Base Materials

Acrylic resin is the most widely material used for the construction of dentures (Ferracane, 2001). It is a thermoplastic and transparent plastic. Chemically, it is the synthetic polymer of PMMA; routinely produced by emulsion polymerization, solution polymerization and bulk polymerization. The material was developed in 1928 in various laboratories and was brought to market in 1933 by Rohm and Haas Company (Wikipedia, 2008a). Polymeric denture base materials are classified into five groups or types according to ISO 1567-2000 (Table 2.2), noticing that type 1 and 2 are the most widely used products

Table 2.2: Classification of Denture Base Polymers According to ISO 1567-2000

Type	Class	Description
1	1	Heat-processing polymers powder and liquid
1	2	Heat-processed (plastic cake)
2	1	Auto polymerized polymers, powder and liquid
2	2	Auto polymerized powder, powder and liquid
3	-	Thermoplastic blank or powder
4	-	Light activated materials
5	-	Microwave cured materials

2.3.2 Compositions of Acrylic Denture Base Materials Type 1 and 2

Type 1 and 2 are the most widely used products (McCabe and Walls, 1998). Both are supplied in a powder and liquid form. The details of the composition are given in the Table 2.3. The major component of the powder is beads of PMMA with diameters up to 100 μ m produced by a process of suspension polymerization in which MMA monomer, containing initiator, is suspended as droplets in water. Starch or carboxy methylcellulose can be used as thickeners and suspension stabilizers to the droplet. The temperature is raised in order to decompose the peroxide and bring about polymerization of the MMA to form beads of PMMA, which after drying form a free flowing powder at room temperature.

PMMA is a clear, glass-like polymer and is occasionally used in this form for denture base construction. Pigments and opacifiers can be incorporated in order to produce a more lifelike denture base. Pink pigments used in denture base resins are traditionally salts of cadmium. These pigments have good color stability and have been shown to leach cadmium from the denture base in only minute amounts. Fears of toxicity of cadmium compounds, however, have led to the gradual replacement of cadmium salts with other safer substances (McCabe and Walls, 1998). PMMA has a good degree of compatibility with human tissue, and can be used for replacement. In addition, it can be color-matched to the patient's teeth and gum tissue (Wikipedia, 2008a).

Table 2.3: Composition of Acrylic Denture Base Materials Type 1 and 2 (McCabe and Walls, 1998)

Material Form		Chemical Composition
Powder	Polymer Initiator Pigment	PMMA beads BPO ($\approx 0.5\%$) Salts of cadmium, iron or organic dyes ($\approx 1\%$)
Liquid	Monomer Cross-linking agent Inhibitor Activator*	MMA EGDMA ($\approx 10\%$) Hydroquinone (trace) <i>NN</i> -dimethyl- <i>p</i> -toluidine ($\approx 1\%$)

*Only in self-curing materials

MMA is a clear, colorless, low viscosity liquid with a boiling point of 100.3°C and a distinct odor which is exaggerated by relatively high vapor pressure at room temperature. It contains some cross-linking agent, and susceptible to free radical addition polymerization. Following mixing of the powder and liquid components and activation, the curing of denture base is due to the polymerization of MMA monomer to form PMMA. The liquid normally contains some cross-linking agent. The substance most widely used is EGDMA. This compound is used to improve the physical properties of the set material.

Hydroquinone, an inhibitor, is used to prolong the shelf life of the liquid component. In the absence of this inhibitor, polymerization of monomer and cross-linking agent would occur slowly, even at room temperature and below, due to the random occurrence of free radicals within the liquid. The source of these free radicals is uncertain, but once formed they cause a slow increase in

viscosity of the liquid and may eventually cause the liquid component to solidify. The inhibitor works by reacting rapidly with radicals formed within the liquid to form stabilized radicals which are not capable of initiating polymerization. One way of reducing the occurrence of unwanted radicals in the liquid is to store the material in a can or in a dark-brown bottle as visible light or ultra-violet radiation may activate compounds which are potentially capable of forming radicals. The activator is present only in those products which are described as self-curing or auto-polymerizing materials and not in heat curing denture base materials. The function of the activator is to react with the peroxide in the powder to create free radicals which can initiate polymerization of the monomer (McCabe and Walls, 2002).

2.3.3 Structure of Acrylic Resins MMA and PMMA

MMA is an organic compound with the formula $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3$. Its structure formula is shown in Figure 2.1. MMA monomer is a clear, transparent liquid. The conversion of monomer MMA to polymer in acrylic resin involves free radical addition polymerization process. The conversion process involves the normal sequence of activation, initiation, propagation and termination.

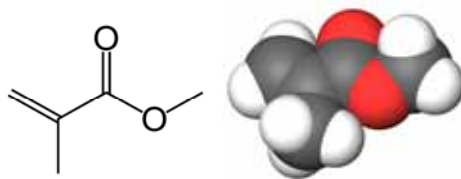


Fig 2.1: Chemical Structure of MMA (wikipedia, 2008b)